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A high-frequency light-induced electron spin resonance study of conjugated polymer/fullerene composites

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Abstract

Light-induced electron spin resonance (LESR) measurements are reported in composites of MDMO-PPV and PCBM, a soluble derivative of C_{60}. After illumination of the sample, two radicals are formed. One is the remaining positive polaron P^+ on the polymer backbone and the other the $C_{61}{}^{\bullet -}$ radical anion. Using high-frequency (95 GHz) LESR, it was possible to separate these two contributions to the spectrum on the basis of their *g*-parameters, and to resolve the *g*-anisotropy of the radicals. The P^+-polaron possesses axial symmetry whereas for $C_{61}{}^{\bullet -}$ a lower, rhombic symmetry was observed.

Keywords: Electron spin resonance; Radicals; Symmetry properties

1. Introduction

The interest in organic donor–acceptor heterojunctions is steadily growing due to their use in active layers of photovoltaic devices. The efficient generation of charge carriers in these materials and their fate after creation are important issues to be addressed. Many studies before already proved the fast (<1 ps) spatial separation [1] of the charge carriers and the stability of the trapping centers.

This paper presents light-induced electron spin resonance (LESR) measurements on composites of conjugated polymers and fullerenes, in which radicals are created by optical excitation in the cavity.

Electron spin resonance (ESR) is a proven technique for the investigation of radical formation. LESR measurements on composites of conjugated polymers and fullerenes were already performed in a conventional X-band (9.5 GHz) spectrometer [2]. The most important findings were the creation of two radicals: the positive polaron P^+ on the polymer and the $C_{61}{}^{\bullet -}$ anion radical on the fullerene.

Their ESR lines were found to overlap in the X-band, and could be distinguished by the different linewidth and saturation behavior.

Furthermore, X-band LESR measurements demonstrated the stability of the trapping states at low temperatures. After switching off the light, the intensity of the LESR lines decreased slightly. The dependency on the light intensity of both light-on and light-off revealed a bimolecular annihilation process.

High-frequency (HF)-LESR can lead to a better understanding of the physics on the molecular scale. On the other hand, HF-LESR can distinguish better between both contributions to the LESR spectrum which are only slightly separated in *g*-value in the X-band. Also it is possible to resolve small *g*-anisotropies of each of the features.

2. Materials and sample preparation

As a conjugated polymer we used poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylene vinylene], hereafter denoted by MDMO-PPV. The absorption and photoluminescence curves, measured at room temperature are shown in Fig. 1. As a comparison, the absorption curve at 77 K is also given. Notice the small red-shift, indicating a better conjugation at lower temperatures. The fullerene used in the study was [6,6]-phenyl-C_{61}-butyricacidmethylester or PCBM, a soluble derivative of C_{60}. Both components were dissolved separately in a 1 wt.% solution of dimethylbenzene (xylene) whereafter they were mixed together in a 1:1 concentration. As a final step, the samples were dried from solution in the ESR sample tubes.

The high-frequency ESR spectrometer operates in the W-band (95 GHz). It consists of a Bruker frequency mixing

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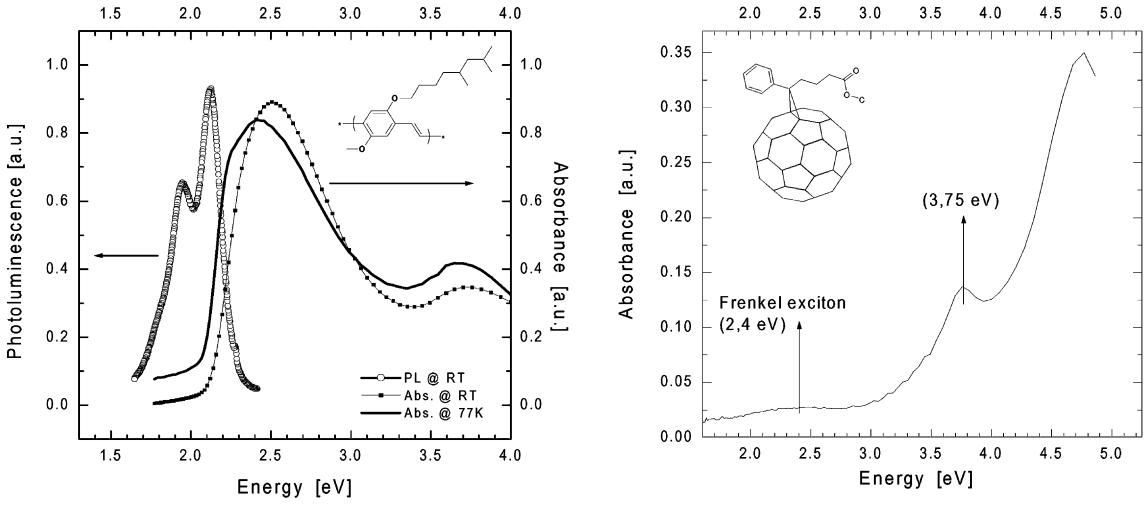

Fig. 1. In the left figure, the photoluminescence and absorption spectra are shown of MDMO-PPV both at room temperature and at 77 K. The right figure shows the absorption spectrum of PCBM. Each of the molecular structures is given in the insets.

microwave source (9.5 GHz + 84 GHz), a Bruker cylindrical cavity and an Oxford 6T superconducting magnet. The low temperature measurements were performed in an Oxford flow cryostat.

The samples were illuminated with the 488 nm (≈2.5 eV) line of an Ar^+ laser. The light was guided to the sample through an optical fiber.

3. W-band LESR spectrum

The first goal of the study was to separate in the spectrum the lines of both the P^+ and the $C_{61}{}^{\bullet-}$ radical. In contrast with the X-band LESR, well separated spectral features can be observed in the W-band measurements. As shown in Fig. 2, these features are attributed to the positive polaron P^+ (labeled by $g_\perp$ and $g_\parallel$) and the $C_{61}{}^{\bullet-}$ radical (labeled by g_x, g_y and g_z).

The positive polaron P^+ radical and the $C_{61}{}^{\bullet-}$ radical have a different saturation behavior. In the X-band, one made use of this property to distinguish between the different contributions in the spectrum. In the W-band, a "fast passage effect" [3] was observed on the P^+-lines, resulting from saturation at higher microwave powers.

Furthermore, HF-LESR resolves the g-anisotropy of both features, revealing the symmetry of the radicals. The axial symmetry of the P^+ indicates that this radical is most likely localized on the phenyl unit of the PPV structure.

The dependence of both contributions in the LESR spectrum from 100 to 160 K was measured. Both show a $1/T$

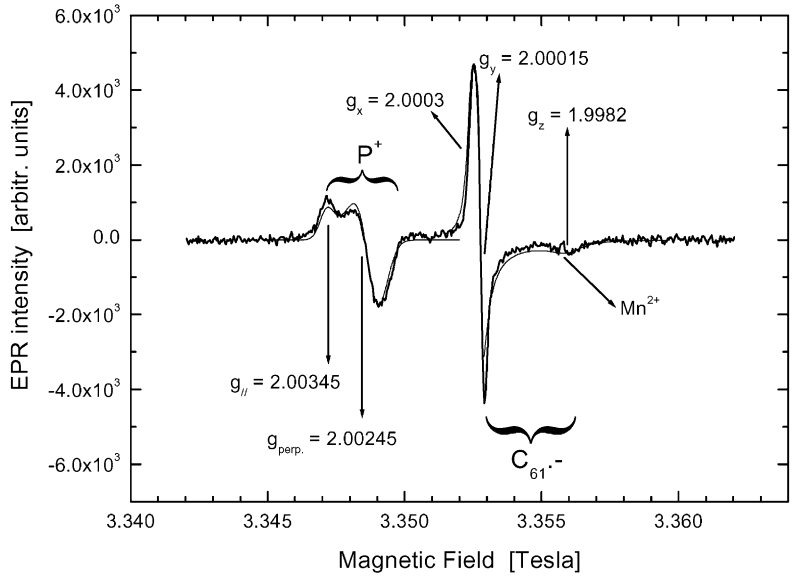

Fig. 2. LESR spectrum of the MDMO-PPV/PCBM composite, showing the fullerene radical ($C_{61}{}^{\bullet-}$), and the positive polaron (P^+). The thin lines are simulations. Weak spurous Mn^{2+} lines, originating from the cavity are indicated in the spectrum.

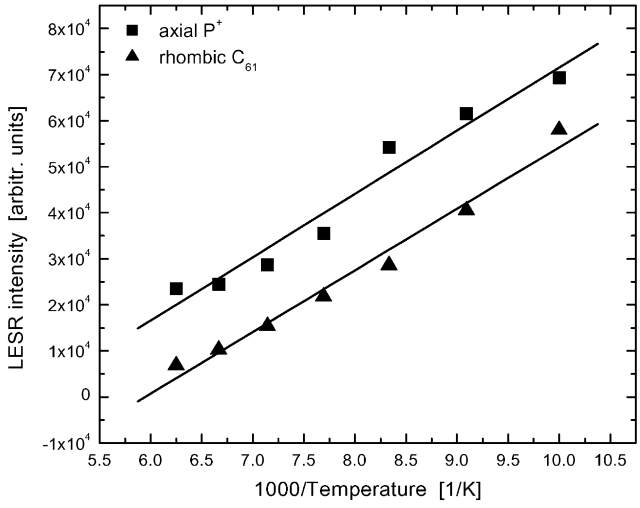

Fig. 3. Temperature dependence of both contributions in the spectrum. The sample was under continuous illumination.

behavior. The parameters of the linear fits in this interval demonstrate that there is not only the Curie law but also another contribution that induces a decrease in the LESR intensities upon increasing temperature. Most likely, this is a thermally activated bimolecular annihilation process (Fig. 3).

To examine the P^+-polaron, one can deliberately create the radical by doping a sample of pure MDMO-PPV with iodine (I_2). The ESR spectrum, however, only reveals one single broader line ($\approx$15 G in comparison with the 5 G fit of the linewidth in the axial powder spectrum). The presence of counter ions leads to broadening of the ESR lines so that the axial symmetry of the P^+ is no longer resolved. Finally, a longer exposure to I_2 leads to a further increase in the broadening of this ESR transition.

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